

Methylbiphenyls

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF MICHIGAN

By

John Carl Pernert

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ACKNOWLEDGMENT

To Professor M. Gomberg, for his assistance and guidance throughout this work, and for the inspiration afforded by his interest, I wish to express my deep gratitude.

JOHN CARL PERNERT

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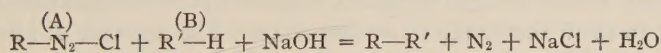
METHYLBIPHENYLS

Recently Gomberg and Bachmann¹ have described a procedure whereby a number of unsymmetrical biaryls, hitherto difficult or impossible of preparation, have been obtained in satisfactory yields.

The literature on methylbiphenyls is not extensive, and the preparation and purification of these hydrocarbons has been very difficult. In some cases the constitutions of the derivatives remain wholly unknown, in others they are not conclusively proved and are open to question. The main purpose of this investigation has been to work out suitable syntheses for a few of these hydrocarbons and to prepare some of the derivatives and obtain convincing proof of their constitutions. In connection with this, we have accumulated a number of facts which permit a further insight into the mechanism of the reactions involved in the general method of synthesizing the unsymmetrical biaryls by the coupling of the diazonium salts.

The Mechanism of the Reaction

According to the procedure recommended by Gomberg and Bachmann, any desired aromatic amine, Component A, is diazotized in aqueous acid solution; Component B, usually immiscible with the aqueous solution, is then added and to the mixture, vigorously stirred, aqueous alkali solution is added drop by drop. When the uncombined acid has been neutralized and the diazonium base begins to be liberated, a vigorous reaction ensues, nitrogen is liberated and a biaryl results, the yield varying from 5 to 40% according to the nature of the two components.

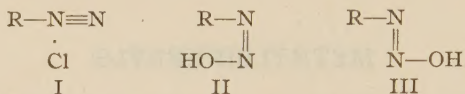


The reactions which occur here are by no means simple ones. Two general types account for the phenomena which we have observed: (a) coupling, with formation of biaryls and polyaryls; (b) oxidation and reduction, with formation of simple compounds, such as azo-derivatives, and tarry mixtures of many complex products.

(a) **Coupling.**—All our evidence indicates that the reaction with which we are dealing is due not to the base which corresponds in structure to the true diazonium salt (I), but is due to the tautomeric modification thereof (II), extremely reactive and feebly acidic in character, that is, the *syn*-diazotic acid. It remains unsettled whether the acid acts in this instance as such or as the anhydride, $(\text{RN}_2)_2\text{O}$, as has been surmised to be

¹ Gomberg and Bachmann, *J. Am. Chem. Soc.*, **46**, 2339 (1924).

the case by Bamberger² who employed these highly explosive substances in their solid state for the synthesis of several biaryls.



The advantages gained by the procedure described by Gomberg and Bachmann over that of Bamberger are: first, the elimination of the necessity for isolating the solid "diazo-anhydrides," obviously a troublesome and highly dangerous task; second, this change permits the reaction to be carried out on an enormously increased scale. The success of the reaction is seen at once to lie in the ability of the non-aqueous liquid, Component B, to extract from the aqueous layer the reactive diazo compound as fast as it is formed. When Component A is a substituted aniline containing negative groups, such as nitro, cyano or halogen, then the *syn*-diazo compound forms a yellow precipitate when alkali is added to the diazonium salt solution and is usually little soluble in water. Basic substituents, such as methyl groups, as a rule increase the solubility in water and also decrease the stability of these *syn*-diazo compounds. Even when the reactive compound is very soluble, the coupling reaction will still be successful if the partition between the aqueous and non-aqueous layers is such that it tends to concentrate in the latter.

We have now found that it is possible, and sometimes advantageous, to carry out the coupling reaction in a distinctly alkaline rather than in a neutral medium, as was done by Gomberg and Bachmann. This tends to keep the diazo compound in the form of the *syn*- or *anti*-diazotate salt, II or III, and prevents the accumulation of much free diazoic acid at a time. The diazotized amine is poured slowly into a mixture containing Component B and a slight excess of sodium hydroxide solution over that required to form the sodium *syn*-diazotate. The amount of alkali differs with the various amines, and the concentration which gives best results must be determined experimentally for the individual cases.

The success of this modified procedure can be explained as follows. Alkalies tautomerize the strongly basic aryl diazonium hydroxides I to acidic forms II and III, which are then able to form salts.³ These acids, however, are usually weak and their salts are, therefore, much hydrolyzed. It is very reasonable to suppose that a solution containing an alkali *syn*-diazotate has, also, some of the reactive hydrolysis product in equilibrium with it. Any substance which can extract this hydrolysis product and react with it must then produce the complete hydrolytic decomposition of the salt, when mixed with the solution. That this is the course of the re-

² Bamberger, *Ber.*, 29, 446 (1896).

³ Hantzsch, *Ber.*, 28, 1735 (1895).

action is indicated by the fact that benzene does not react with solid potassium benzene *syn*-diazotate. When water is added to the mixture reaction immediately begins. Only certain types of amines, however, can thus be successfully brought into the reaction through their sodium *syn*-diazotates. These include aniline and the toluidines. As a rule, those amines containing negative substituents are not suitable, partly because they are readily converted into the less reactive *anti*-diazotates, partly because they form stronger *syn*-diazoic acids, the salts of which are then less readily hydrolyzed.

Oxidation and Reduction.—Besides the coupling reaction, which is usually the principal one, there also are reactions whereby the diazo group is replaced by hydrogen. In many cases the amount of reduction cannot be easily determined; in some, for example, the brominated toluidines, the product so formed, bromotoluene, can be easily isolated and identified. When we coupled 2-methyl-4-bromo-aniline with benzene we found that 3-bromotoluene was produced in an amount equivalent to 10% of the amine used. An isomer, 4-methyl-2-bromo-aniline, was reduced under similar conditions to the extent of 6%.

Reactions whereby diazo groups may be replaced by hydrogen have long been known. In all cases reduction has been accomplished by strongly reducing substances such as zinc dust, stannous chloride or alcohol. So far as we know, the above reaction, wherein the diazo group is reduced by reagents commonly considered relatively weak in that respect, has not hitherto been observed. The reaction must involve either the dehydrogenation and decomposition of a part of Component A or of Component B, perhaps both. Possibly such reactions may account for the formation of the complex, tarry products invariably formed in these reactions.

Azo compounds, always present in the reaction mixtures, result from less complete reduction of the diazo compounds. We have been able to isolate an azo derivative from one series of coupling reactions, namely, those in which 4-toluidine was used as Component A. Whether benzene or toluene was used as Component B we found that 4,4'-dimethyl-azo-benzene was formed. That a symmetrical compound is obtained, independently of the nature of Component B, indicates that the reaction whereby it is formed involves a partial reduction and simultaneous coupling of two molecules of 4-diazo-toluene. $2\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl} + 2\text{NaOH} + \text{H}_2 = \text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{N}=\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3 + \text{N}_2 + \text{NaCl} + 2\text{H}_2\text{O}.$

Preparation of 4-Methylbiphenyl from 4-Toluidine and Benzene

One mole (107 g.) of 4-toluidine was dissolved in 185 cc. of hydrochloric acid (d., 1.2), the solution cooled by the addition of ice, and diazotized by the slow addition of a slight excess of sodium nitrite dissolved in water. The temperature was kept low, but a large excess of ice was avoided. This solution was added, during the course of two or three minutes, to a vigorously stirred mixture containing 275 cc. of sodium hydroxide solution (400 g. in 1 liter), 600 cc. of benzene, and ice in sufficient amount to

cool the mixture to about 5°. A small part of the benzene was kept frozen by the addition from time to time of a little ice. When all of the diazo solution had been added a vigorous reaction began, the mixture became yellow, nitrogen was evolved, and the temperature gradually rose. A temperature higher than about 5° was found to lead to the formation of a dark-brown reaction mixture and to decrease the yield of biaryl. The stirring was continued for about five hours. The addition of ice was discontinued after the first hour and the temperature allowed to rise to that of the room.

Two procedures were used in separating the 4-methylbiphenyl from the other products of the reaction; steam distillation and vacuum distillation. The former procedure is more satisfactory when small amounts of material are to be handled, the latter saves time when the reactions are carried out on a comparatively large scale.

Steam Distillation.—When the reaction, as described above, was at an end the benzene layer, then very dark, was separated from the strongly alkaline aqueous layer. The benzene was distilled, and the black, tarry residue steam distilled, with the flask in an oil-bath at 150–175°. The first portion of the distillate was nearly pure 4-methylbiphenyl, solid and only slightly colored. When this was almost completely removed, an oil began to distil, the quantity increasing rapidly at a still higher temperature of the oil-bath. When the temperature of the oil-bath had reached 240°, crystals again appeared in the condenser and in the upper parts of the distilling flask. The three portions of the distillate were collected separately.

The 4-methylbiphenyl was redistilled at atmospheric pressure, b. p., 267–268°, yielding 38 g. of a pale yellow liquid, which soon solidified to a mass of large, glistening crystals; yield, 22% of that calculated on the amount of amine, 107 g., used in the reaction. When the crude product was first dissolved in alcohol containing some hydrogen chloride and the solution warmed with zinc or tin for a short time, in order to reduce the azo compounds, a perfectly colorless product was obtained. This hydrocarbon is very soluble in organic solvents. It is best crystallized from methyl alcohol, from which it separates in pearly flakes which melt at 47.7°. A melting point⁴ of 49–50° for this compound has been recorded, but we have been unable to attain this value even after many recrystallizations.

The crystalline product which constituted the highest-boiling fraction weighed 0.3 g. Crystallization from glacial acetic acid gave small, almost colorless flakes, which melted at 249–250°. From nitrobenzene, small, compact prisms are formed. This is a hydrocarbon (C, 92.88%; H, 6.84%). Its composition, its properties, and method of preparation make it almost certain that it is 1,4-di(4-tolyl)benzene, $\text{CH}_3\text{C}_6\text{H}_4\text{--C}_6\text{H}_4\text{C}_6\text{H}_4\text{CH}_3$.

The oil which composed the middle fraction was a mixture from which we were not able to isolate any crystalline compounds. It probably contains isomeric di(4-tolyl)benzenes.

Vacuum Distillation.—The reaction products resulting from the interaction of 3 moles (321 g.) of 4-toluidine with benzene was dried over calcium chloride and distilled in a vacuum. At 20 mm. pressure a fraction boiling at 145–153° was collected. This weighed 109 g. and was almost pure 4-methylbiphenyl. Two fractions of approximately equal weight, and totaling 33 g., were collected at higher temperatures. The first was an oil, from which an orange-red substance gradually crystallized. When recrystallized from alcohol it formed flat needles; m. p., 143–144°; yield, 1.2 g. It was proved to be 4-azotoluene. From the second fraction there crystallized 1.5 g. of 1,4-di(4-tolyl)benzene.

We have oxidized our methylbiphenyl to the corresponding phenylbenzoic acid by

⁴ Kliegl and Huber, *Ber.*, **53**, 1655 (1920).

means of aqueous solutions of potassium permanganate,⁵ and have obtained almost quantitatively 4-phenylbenzoic acid. For further identification of the product, the same acid was prepared from 4-cyanobiphenyl.⁶ Crystallization from carbon tetrachloride produced needles that melted at 223°.

Preparation of 2-Methylbiphenyl from 2-Toluidine and Benzene

Bamberger has shown⁷ that alkalies react with diazotized 2-toluidine with formation of indazole. When we coupled 2-toluidine with benzene, by our modified procedure, we obtained 2-methylbiphenyl as well as indazole.

Fifty-four g. (0.5 mole) of 2-toluidine was brought into reaction with benzene exactly as has been described for 4-toluidine, with the single exception that 2.4 equivalents of sodium hydroxide was used instead of 2.75, as in that case. The proportions of all other reagents remained unchanged. Distillation of the benzene solution gave 6.8 g. of 2-methylbiphenyl, which corresponds to a yield of 8%.

Anal. Calcd. for C₁₃H₁₂: C, 92.85; H, 7.15. Found: C, 92.52; H, 7.01.

A part of the 2-methylbiphenyl was oxidized to 2-phenylbenzoic acid by neutral permanganate; m. p., 110°.⁵

Coupling of Aniline with Toluene.—Ninety-three g. (1 mole) of aniline was diazotized and brought into reaction with toluene under the conditions described for the preparation of 4-methylbiphenyl, except that instead of 2.75 equivalents of sodium hydroxide, only 2.4 equivalents was used and the temperature at which the reaction mixture was maintained was initially a little below 0°. This low temperature was possible in this case because of the lower freezing point of Component B.

Steam distillation of the tarry residue after distilling the toluene gave 35 g. of an oily liquid colored by small amounts of azo compounds. The oil was fractionated at atmospheric pressure. The total yield of biaryls corresponded to 16% and consisted of a mixture of 2-methylbiphenyl and 4-methylbiphenyl. A fraction weighing 8 g., which boiled at 255–258°, proved to be almost pure 2-methylbiphenyl. Oxidation converted it to 2-phenylbenzoic acid. The fraction boiling at 265–270° contained much 4-methylbiphenyl, as was shown by the production of large amounts of 4-phenylbenzoic acid, when a portion of it was oxidized. We were, however, not able to separate from this mixture the two hydrocarbons themselves in the solid state. Others have failed to separate similar mixtures⁸ and this fact accounts for many of the inaccurate descriptions of 4-methylbiphenyl which are in the literature.

A still higher-boiling fraction, amounting to several grams, doubtless consisted largely of a mixture of isomeric methyl-diphenylbenzenes.

Bromination of 4-Methylbiphenyl

4-Bromo-4'-methylbiphenyl.—Carnelley and Thomson⁹ brominated samples of impure 4-methylbiphenyl. The principal product isolated by them was assigned the structure as either 2- or 3-bromo-4-methylbiphenyl.

⁵ Jacobson, *Ber.*, **28**, 2552 (1898).

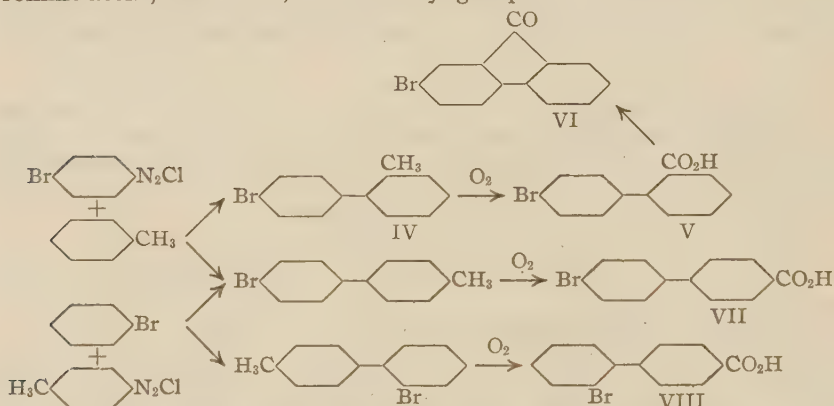
⁶ Ref. 2, p. 2343.

⁷ Bamberger, *Ann.*, **305**, 340 (1899).

⁸ Möhlau and Berger, *Ber.*, **26**, 1997 (1893). Bamberger, *Ber.*, **30**, 369 (1897). Knowles, *J. Am. Chem. Soc.*, **43**, 896 (1921).

⁹ Carnelley and Thomson, *J. Chem. Soc.*, **47**, 588 (1885); **51**, 87 (1887).

We find, however, that the bromine atom and the methyl group are not in one and the same benzene ring as has been inferred by Carnelley and Thomson. We were able to prove this by isolating the identical compound from the reaction mixture obtained when we coupled 4-bromoaniline with toluene; likewise when we coupled 4-toluidine with bromobenzene. The first method of preparation proves the position of the bromine atom; the second, of the methyl group.



The bromo compound thus obtained proved also identical with the one which is formed when 4-methylbiphenyl is brominated by means of bromine. On oxidation the bromo compound gives first 4-bromo-4'-carboxybiphenyl and not bromoterephthalic acid, as was supposed by Carnelley and Thomson; then, on further oxidation, 4-bromobenzoic acid is formed.

To 21 g. of 4-methylbiphenyl in 50 cc. of carbon tetrachloride 20 g. of bromine was added, and the mixture after standing for 12 hours was heated almost to the boiling point for a half hour. When the solution had cooled, the bromo-methylbiphenyl crystallized; yield, 20.5 g., or 67%. After two crystallizations from alcohol or benzene, the substance melted at 133° and boiled at 314–315°. It is rather soluble in benzene, almost insoluble in cold alcohol and in carbon tetrachloride. It corresponds in all respects with the bromo compound which Carnelley and Thomson described except for the slightly higher melting point.

Oxidation of 4-Bromo-4'-methylbiphenyl to 4-Bromo-4'-carboxybiphenyl.—One g. of the 4-bromo compound was heated with 20 cc. of glacial acetic acid to about 90°; 2 g. of finely powdered chromic acid anhydride was added, little by little, and the mixture stirred occasionally during 15 hours. When the reaction mixture was diluted with water, there precipitated a voluminous mass of a product which weighed 1.1 g. It consisted of microscopic needles and had the appearance of cotton. Crystallization from boiling nitrobenzene gave microscopic needles; m. p., 304°.

Anal. Calcd. for C₁₃H₉O₂Br: Br, 28.8. Found: 29.0.

This acid is slightly soluble in organic solvents, in cold alkalis, and in cold aqueous ammonia, more soluble in hot alkalis. It resembles bromo-terephthalic acid rather closely, especially as the latter also melts at 304°. On further oxidation it gives *p*-bromobenzoic acid, and this is confirmatory evidence that the biaryl is 4-bromo-4'-methylbiphenyl.

Coupling of 4-Bromo-aniline with Toluene.—Seventeen and a half g. of 4-bromo-aniline (0.1 mole) was diazotized in the usual way. After the addition of 150 cc. of toluene the mixture was vigorously stirred, and a 30% solution of sodium hydroxide added, drop by drop, until an alkaline reaction was attained. Steam distillation gave 7 g. of biaryls, corresponding to a yield of 28%. About a gram of this collected in the condenser as a solid. After being crystallized from alcohol it melted at 133° and was identical with the bromo compound obtained by direct bromination of 4-methylbiphenyl.

The liquid portion of the product constituted about two-thirds of the total and consisted largely of 4-bromo-2'-methylbiphenyl. It was fractionated at atmospheric pressure; b. p., 303–305°. Neutral permanganate oxidized it very slowly to the corresponding acid, namely, 4-bromo-2'-carboxylbiphenyl which was converted into 2-bromofluorenone (VI), by the action of aluminum chloride on the acid chloride.¹⁰ The fluorenone crystallized from alcohol in long, yellow needles and melted at 149°. The melting point of this compound is given as 134° in the literature.¹¹

Coupling of 4-Toluidine with Bromobenzene and with Chlorobenzene.—Twenty-one g. (0.2 mole) of 4-toluidine was brought into reaction with bromobenzene exactly as described for the preparation of 4-methylbiphenyl, the temperature being kept near 0°. Steam distillation gave 11 g. of a mixture of bromomethylbiphenyls. This corresponds to a 22% yield. From the higher-boiling portion of the fractionated oil, there crystallized about 1 g. of 4-bromo-4'-methylbiphenyl. The fraction boiling at 301–303°, a colorless oil, weighed 3 g. and was almost pure 2-bromo-4'-methylbiphenyl.

When 4-toluidine was coupled with chlorobenzene, in a way exactly similar to that described for the coupling with bromobenzene, there were obtained 4-chloro-4'-methylbiphenyl, m. p. 122°, and the 2-chloro-4'-methylbiphenyl, b. p. 288–290°. Each of the two was analyzed for chlorine and found to contain 17.24% and 17.31%, respectively, against 17.50% calculated.

2-Bromo-4'-carboxylbiphenyl.—Neutral permanganate oxidizes 2-bromo-4'-methylbiphenyl to the corresponding acid, but the use of chromic acid in glacial acetic is more convenient and just as satisfactory. 2-Bromo-4'-carboxylbiphenyl crystallizes from glacial acetic acid in colorless needles; m. p., 242°. It sublimes easily, dissolves in cold dil. aqueous ammonia and is more soluble in the usual organic solvents than its isomer, 4-bromo-4'-carboxylbiphenyl.

Anal. Calcd. for $C_{13}H_9O_2Br$: Br, 28.8. Found: 29.05.

Nitration of 4-Methylbiphenyl

Carnelley¹² nitrated a sample of partially purified 4-methylbiphenyl, and obtained a mononitro-derivative which melted at 141°. He did not know the structure of this compound. Kliegl and Huber,⁴ arguing by analogy from a rather complex reaction, assigned to this compound the probable constitution as that of 4-nitro-4'-methylbiphenyl. Hirsch¹³ also came to the same conclusion, but here again the proof of the structure of the compounds is not complete.

We have repeated Carnelley's experiments, reduced the nitro to the amino compound, and have converted our amino-4-methylbiphenyl into the corresponding bromo derivative through the Sandmeyer reaction. The

¹⁰ Scholl and Seer, *Ann.*, **394**, 111 (1912).

¹¹ Schmidt and Bauer, *Ber.*, **38**, 3751 (1905).

¹² Carnelley, *J. Chem. Soc.*, **29**, 20 (1876).

¹³ Hirsch, *Ger. pat.* 58,001 (1891).

product proved identical with that described above, namely, 4-bromo-4'-methylbiphenyl. Nitration, therefore, has occurred in the 4-position.

We have obtained 4-nitro-4'-methylbiphenyl also by coupling 4-toluidine with nitrobenzene. Others have found¹⁴ that, in such cases, the usual rule in respect to the directive influence of substituents in the benzene nucleus does not hold. Coupling takes place in Position 4, with respect to the nitro group, instead of 3, as is usually the case in other chemical reactions.

Preparation of 3-Methylbiphenyl from 3-Toluidine and Benzene

Good yields of 3-methylbiphenyl can be obtained when 3-toluidine is coupled with benzene, either by the general method in a neutral solution or by our modified procedure in an alkaline solution. The results obtained by the latter are somewhat the better.

Eleven g. of 3-toluidine was coupled with benzene exactly as in the case of the preparation of 4-methylbiphenyl from 4-toluidine and benzene; yield, 4.5 g., or 28%; b. p., 267–269°.

Anal. Calcd. for $C_{13}H_{12}$: C, 92.85; H, 7.14. Found: C, 92.90; H, 7.12.

A part of the 3-methylbiphenyl was oxidized and gave an acid which melted at 166°. It proved to be identical in all respects with the 3-phenylbenzoic acid prepared from 3-cyanobiphenyl.¹⁵

Coupling of 4-Toluidine with Toluene; 4,4'-Dimethylbiphenyl and 2,4'-Dimethylbiphenyl

One hundred and seven g. (1 mole) of 4-toluidine was diazotized and brought into reaction with toluene. The temperature, at first, was kept near 0°. Steam distillation (oil-bath at 200–225°) gave 43 g. of distillate. Thirty-five g. of this boiled at 270–300° at atmospheric pressure. Careful fractionation gave 10 g. of a colorless liquid, 2,4'-dimethylbiphenyl, b. p. 273–276°, and 5 g. of a liquid, b. p. 286–294°, from which about 2 g. of 4,4'-dimethylbiphenyl, m. p. 121°, was separated. This latter corresponded in every respect with a sample of the same hydrocarbon prepared¹⁶ by the Ullmann reaction by heating 4-iodo-toluene with finely divided copper.

The 2,4'-dimethylbiphenyl was analyzed.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.30; H, 7.69. Found: C, 92.57; H, 7.56.

A neutral permanganate solution gradually oxidized our crude 2,4'-dimethylbiphenyl to the corresponding dicarboxylic acid. This acid was found to be slightly soluble in water and could be separated in this way from the less soluble 4,4'-biphenyl-dicarboxylic acid, which was also present in small amount. The acid was crystallized from a mixture containing equal parts of acetic acid and water. It melts at 265°, and not at 252°. ¹⁷ According to the literature, the silver salt of this acid melts at 235–237°. We found it to be infusible, stable to a comparatively high temperature, finally decomposing with deposition of metallic silver.

For purposes of further identification, the acid was heated to the point of sublima-

¹⁴ Kühling, *Ber.*, **29**, 165 (1896). Ref. 2, p. 2341.

¹⁵ Ref. 2, p. 2343.

¹⁶ Ullmann and Meyer, *Ann.*, **332**, 44 (1904).

¹⁷ Reuland, *Ber.*, **22**, 3018 (1889).

tion. It lost water and was converted almost quantitatively into 2-fluorenonecarboxylic acid. Several resublimations gave the product pure, in the form of bright yellow, fern-like crystals, which sublimed above 340° without melting. The acid corresponds in all respects with that described in the literature.¹⁸

Coupling of 4-Methyl-2-bromo-aniline and of 2-Methyl-4-bromo-aniline with Benzene

We have previously pointed out that amines differ greatly with respect to the results which they give when used in the coupling reaction. We found that 4-methyl-2-bromo-aniline and the isomer 2-methyl-4-bromo-aniline resemble the halogenated anilines when used in the coupling reaction. While the toluidines give distinctly better results when they are allowed to react as the sodium *syn*-diazotate, their halogen derivatives, on the other hand, gave very poor yields under similar conditions. Using the general procedure, however, we obtained satisfactory results.

One hundred and eleven g. (0.5 mole) of 4-methyl-2-bromo-aniline hydrochloride was suspended in 75 cc. of concd. hydrochloric acid, ice was added, and the amine diazotized. Four hundred cc. of benzene was added, and to the vigorously stirred mixture sodium hydroxide solution was very gradually added until the reaction became permanently alkaline. Steam distillation gave 37 g. of an oil. This was distilled at atmospheric pressure. A fraction weighing 5 g. boiled at $180\text{--}185^{\circ}$, and was proved to be 3-bromotoluene. The higher-boiling fraction, 30 g. of colorless oil, b. p. $301\text{--}303^{\circ}$, was 4-methyl-2-bromobiphenyl; yield, 25%.

Anal. Calcd. for $C_{13}H_{11}Br$: Br, 32.37. Found: 33.0.

The coupling of 2-methyl-4-bromo-aniline with benzene was carried out exactly as in the case of its isomer. The crude product was an oil which weighed 21 g. Fractionation produced 8.5 g. of 3-bromotoluene, which corresponds to the reduction of about 10% of the amine, and 9 g. of 2-methyl-4-bromobiphenyl, b. p. $303\text{--}304^{\circ}$, corresponding to a 7.5% yield.

Anal. Calcd. for $C_{13}H_{11}Br$: Br, 32.37. Found: 31.9.

3-Bromo-4-phenylbenzoic Acid and 2-Phenyl-5-bromobenzoic Acid.—Neutral permanganate readily oxidizes the two isomeric bromo-biaryls to the corresponding acids. The first mentioned acid is little soluble in organic solvents. It was crystallized from boiling nitrobenzene, and was obtained in colorless needles which melt at $215\text{--}216^{\circ}$.

Anal. Calcd. for $C_{13}H_9O_2Br$: Br, 28.8. Found: 28.95.

The second mentioned acid dissolves very slightly in boiling water. It may be crystallized from glacial acetic acid; m. p., $161\text{--}162^{\circ}$. When distilled, 2-phenyl-5-bromobenzoic acid loses water and slowly becomes converted into the yellow compound, 2-bromofluorenone (VI). This proves the constitution of the acid, and therefore also of the biaryl.

Some Derivatives of 4-(4-Tolyl)triphenylmethyl

Several free radicals of the triarylmethyl type, containing the biphenyl nucleus, have been prepared and studied by Schlenk and others. No homologs are reported in the literature. We have now prepared two new triarylmethyls which have, as one of the three aryl groups, the 4-methyl-

¹⁸ Fortner, *Monatsh.*, **25**, 451 (1904).

biphenyl group, namely, 4-(4-tolyl)triphenylmethyl and phenyl- α -naphthyl-4-(4-tolyl-phenyl)methyl.

The radicals showed all the well known properties characteristic of compounds of this class, and were found to be sufficiently stable so that their solutions could be kept for days, even exposed to bright sunlight for many hours, with no noticeable change. Unfortunately, it has proved impossible to isolate these radicals in crystalline form and we were, therefore, prevented from determining the degree to which they are monomolecular.

4-(4-Tolyl)benzophenone, $(\text{H}_3\text{C}.\text{C}_6\text{H}_4.\text{C}_6\text{H}_4).\text{CO}.\text{(C}_6\text{H}_5)$.—This ketone was prepared from benzoyl chloride and 4-methylbiphenyl in carbon disulfide by the Friedel and Crafts' reaction. The ketone was crystallized from benzene. White flakes, melting at 129–130°, were obtained; yield, 68%. The substance is soluble in hot alcohol or benzene, almost insoluble in cold alcohol.

Anal. Calcd. for $\text{C}_{20}\text{H}_{16}\text{O}$: C, 88.24; H, 5.88. Found: C, 88.13; H, 6.07.

Mol. wt. Calcd.: 272. Found: 265, 274.

On reduction with sodium amalgam and alcohol, the ketone formed 4-(4-tolyl)-benzhydrol which was obtained as long, silky needles; m. p., 96.5–97°.

Anal. Calcd. for $\text{C}_{20}\text{H}_{18}\text{O}$: C, 87.59; H, 6.57. Found: C, 87.80; H, 6.44.

4-(4-Tolyl)triphenylcarbinol, $(\text{H}_3\text{C}.\text{C}_6\text{H}_4.\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C}(\text{OH})$.—The carbinol was prepared from 4-(4-tolyl)benzophenone and phenylmagnesium bromide; towards the end of the reaction ether was displaced by benzene as the solvent. Twelve g. of the ketone gave 15 g. of nearly pure carbinol, corresponding to 95% of the calculated yield. After crystallization from benzene, it was white, and melted at 95–96°. The substance is rather soluble in benzene and practically insoluble in cold petroleum ether.

Anal. Calcd. for $\text{C}_{26}\text{H}_{22}\text{O}$: C, 89.14; H, 6.29. Found: C, 89.39; H, 6.20.

Mol. wt. Calcd.: 350. Found: 346.

With concd. sulfuric acid the carbinol gives an intense red-violet color, which is distinctly different from that given by 4-phenyl-triphenylcarbinol.

Benzophenone dichloride and 4-methylbiphenyl react in the presence of aluminum chloride, ferric chloride or stannic chloride, with formation of this same carbinol, but yields are inferior and the material is less pure than when obtained by the Grignard reaction.

We proved the structure of our carbinol made from the 4-(4-tolyl)benzophenone by isolating an identical product from the interaction of benzophenone and the Grignard reagent from 4-bromo-4'-methylbiphenyl. We have found it difficult to prepare the Grignard reagent from 4-bromo-4'-methylbiphenyl, either by the usual procedure or by various modifications of it. Fortunately we were able to isolate a small amount of carbinol from the reaction mixture obtained in one such experiment and to show that it is identical with that prepared from 4-(4-tolyl)benzophenone. This proves that the structure of our ketone, from methylbiphenyl and benzoyl chloride, is actually as has been implied.

4-(4-Tolyl)triphenylmethyl Chloride, $(\text{H}_3\text{C}.\text{C}_6\text{H}_4.\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C}.\text{Cl}$.—Five g. of the completely purified carbinol was dissolved in the least possible amount of hot benzene. The solution was quickly cooled and diluted with 5 cc. of absolute ether, followed by 2 cc. of acetyl chloride. After warming the solution to the boiling point of the ether for a minute or two, 20 cc. of petroleum ether (40–50°) was added, and the mixture, carefully protected from moisture, set aside for 24 hours. The chloride crystallized in colorless prisms; yield, 5.1 g., or 96%; m. p., 122°.

Anal. Calcd. for $C_{22}H_{21}Cl$: Cl, 9.63. Found: Cl, 9.57, 9.65.

Mol. wt. Calcd.: 368. Found: 364, 365.

The chloride when boiled with zinc in glacial acetic acid is quantitatively reduced to 4-(4-tolyl)triphenylmethane; m. p., 131°.

Anal. Calcd. for $C_{26}H_{22}$: C, 93.41; H, 6.59. Found: C, 93.33; H, 6.36.

Mol. wt. Calcd.: 334. Found: 328.

The chloride dissolves in absolute methyl alcohol and reacts with it to form the methyl ether; m. p., 110°. The corresponding ethyl ether melts at 130–131°.

Anal. Calcd. for $C_{27}H_{24}O$: C, 89.01; H, 6.59. Found: C, 88.91; H, 6.94.

Calcd. for $C_{28}H_{26}O$: C, 88.89; H, 6.88. Found: C, 88.60; H, 6.95.

4-(4-Tolyl)triphenylmethyl and the Peroxide, $((H_3C.C_6H_4.C_6H_4)(C_6H_5)_2C)_2O_2$.—Molecular silver reacts readily with the triarylmethyl chloride in benzene, with the formation of an orange-red solution of 4-(4-tolyl)triphenylmethyl. When exposed to air the solution is rapidly decolorized and when the solvent is evaporated the peroxide crystallizes. The peroxide can be obtained pure by washing with ether and the amount usually corresponds to a 73% yield. The peroxide melts, with decomposition, at 169–170°.

Anal. Calcd. for $C_{52}H_{42}O_2$: C, 89.40; H, 6.02. Found: C, 89.34; H, 6.20.

With iodine, a freshly prepared solution of the radical reacts until 44% of the calculated amount of halogen has been taken up.

We attempted to prepare the radical in the solid, crystalline state, in the usual manner. When a solution in benzene was evaporated under reduced pressure, a colorless, pasty product resulted which we were not able to crystallize from the usual solvents. The radical was very soluble in most solvents, but only slightly soluble in petroleum ether. It may be mentioned that Schlenk failed in his attempts to crystallize the closely related free radical, 4-phenyl-triphenylmethyl.

In some cases the degree of dissociation of the hexaryl ethane into free radicals can be measured by the indirect method, that is, the triarylmethyl chloride is allowed to react with the silver in the molecular-weight apparatus. We found that we could not obtain good results by the indirect method on account of the comparatively slow reaction between our triarylmethyl chloride and silver. During the time necessary to complete the reaction the other errors had increased to such an extent that the results obtained were of little value.

Phenyl- α -naphthyl-4-(4-tolyl-phenyl)carbinol, $(C_6H_5)(C_{10}H_7)(H_3C.C_6H_4.C_6H_4)-C(OH)$.— α -Bromonaphthalene was converted into the Grignard reagent, the ethereal solution of this decanted into a solution of 4-(4-tolyl)benzophenone in dry benzene and the benzene solution refluxed for two hours. The reaction mixture was decomposed in the usual manner. The carbinol contained benzene of crystallization, and melted at 130–135°, with loss of benzene. The dried carbinol was crystallized from carbon tetrachloride and obtained in small, colorless flakes free from solvent of crystallization; m. p., 186°.

THE CHLORIDE, THE METHANE AND THE PEROXIDE.—The chloride was prepared by the usual method and was recrystallized from carbon tetrachloride; m. p., 192°. From benzene it crystallizes with 1 molecule of solvent of crystallization.

Anal. Calcd. for $C_{30}H_{23}Cl.C_6H_5$: C_6H_5 , 15.73; Cl, 7.15. Found: C_6H_5 , 17.16; Cl, 7.00, 7.02.

The chloride is readily reduced to the corresponding methane when boiled with zinc in acetic acid; m. p., 171°.

Anal. Calcd. for $C_{30}H_{24}$: C, 93.75; H, 6.25. Found: C, 93.43; H, 6.17.

A solution of 0.2 g. of the chloride in 10 cc. of benzene was shaken for three hours

with 0.2 g. of molecular silver. The resulting solution of the free radical was intensely colored; thick layers were red-brown and thin layers, greenish-yellow. The solution was quickly decolorized when it was exposed to air, only a faint yellow color persisting. Evaporation of the decolorized solution gave the peroxide. After being washed with ether it was colorless and melted with decomposition at 128–129°.

Anal. Calcd. for $C_{60}H_{46}O_2$: C, 90.24; H, 5.77. Found: C, 90.50; H, 5.96.

This investigation was accomplished with the aid of the National Aniline and Chemical Company Fellowship. We take this opportunity to express our thanks for this assistance.

Summary

1. The coupling of diazonium salts with aromatic hydrocarbons and derivatives has been further investigated and the reaction applied in the synthesis of several biaryls. It has been ascertained in which instances the coupling phase of the operation is best approached from the acid side and in which best from the alkaline side. Through the isolation of some byproducts more light has been thrown on the nature of this complex reaction.

2. The *ortho*-, *meta*-, and *para*-toluidines have been coupled with benzene and gave 2-methyl-, 3-methyl- and 4-methylbiphenyl in yields of 8, 28 and 22%, respectively. Several other coupling syntheses of more complex biaryls are described in this paper.

3. The hitherto uncertain constitution of the bromo and the nitro derivatives of 4-methylbiphenyl has been definitely established.

4. Several new acids have been prepared by partial oxidation of our methylbiphenyl derivatives. From two of these, fluorenone derivatives were prepared in excellent yields. The coupling reaction seems to offer great promise for the preparation of such derivatives.

5. Two new triarylmethyls have been prepared, containing each 4-methylbiphenyl as one of the three aryl groups.

